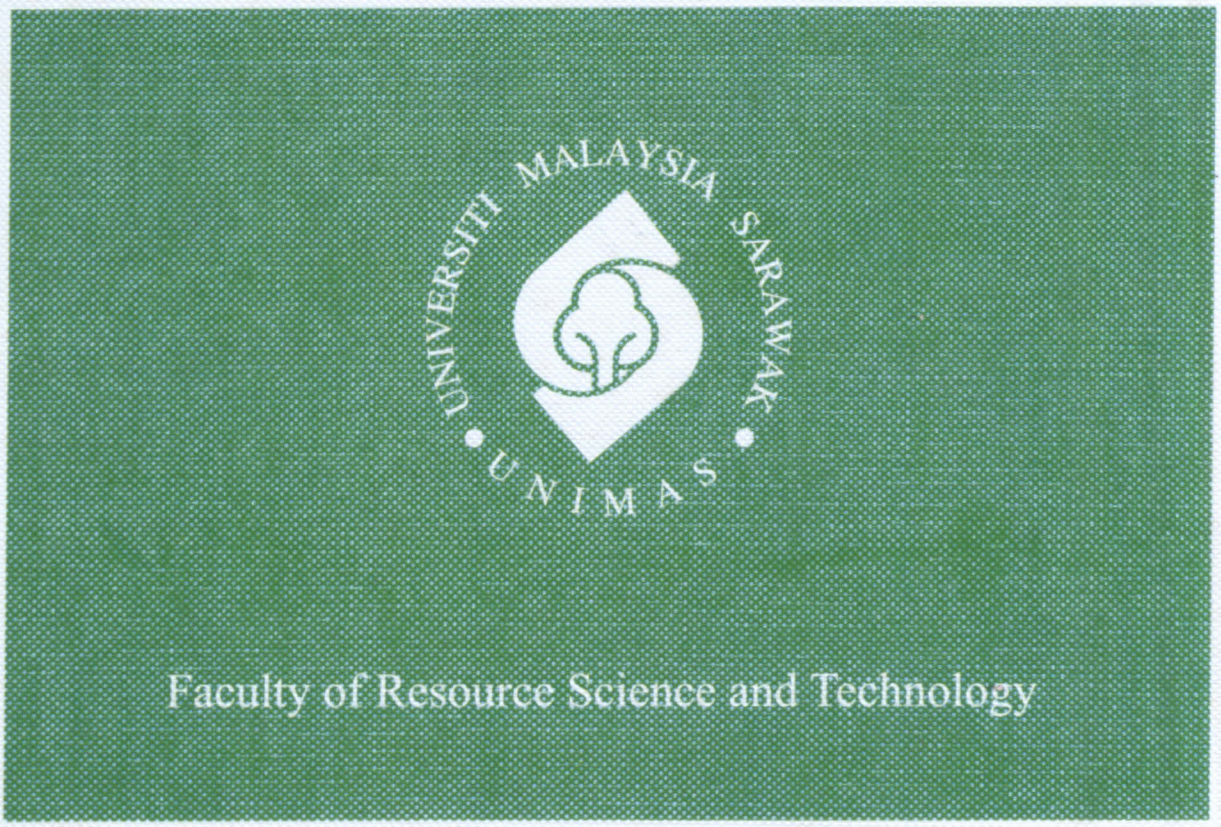

VALUE-ADDED UTILIZATION OF CELLULOSE DERIVED FROM PAPER WASTE: DEPOLYMERIZATION OF CELLULOSE

Lim Hui Yin

Bachelor of Science with Honours
(Resource Chemistry)
2014

UNIVERSITI MALAYSIA SARAWAK

Grade: _____

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Final Year Project Report ☑

Masters ☐

PhD ☐

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I LIM HUI YIN , 33846 , FACULTY OF RESOURCE SCIENCE AND TECHNOLOGY

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Value-added Utilization of Cellulose Derived from Paper Waste:

Depolymerization of Cellulose

Lim Hui Yin 33846

This project is submitted in partial fulfillment of the
requirements for the degree of Bachelor of Science with Honors
(Resource Chemistry)

Supervisor: Professor Dr. Pang Suh Chem

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DECLARATION

I, Lim Hui Yin, final year student of Resource Chemistry hereby declare that this thesis entitle "Value-added Utilization of Cellulose Derived from Paper Waste Depolymerization of Cellulose" is my own work and effort with this guidance of my supervisor, Professor Dr. Pang Suh Chem. This thesis has not been submitted for any other degree, university or institution of higher learning.

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Lim Hui Yin

Program of Resource Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

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LIST OF ABBREVIATIONS

NaCl	Sodium Chloride
DP	Degree of polymerization
TFA	Trifluoroacetic acid
MSW	Municipal Solid Waste
EPA	Environmental Protection Agency
[bmim] Cl	1-butyl-3-methylimidazolium chloride
HPA	heteropolyacid
$CuCl_2$	Copper (II) chloride
$PdCl_2$	Palladium (II) chloride
$CrCl_2$	Chromium (II) chloride
$CrCl_3$	Chromium (III) chloride

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Value-added Utilization of Cellulose Derived from Paper Waste:

Depolymerization of Cellulose

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ABSTARCT

Depolymerization of cellulose is the critical step to breaking down the cellulose into different chain lengths of oligomers. Cellulose depolymerized using salt-assisted organic-acid-catalysis had been characterized as a green and cost-effective approach. The inexpensive sodium chloride (NaCl) with oxalic acid as catalyst was introduced into a reflux system to perform an acid-catalyzed depolymerization of cellulose under mild reactions conditions (105-150^{0}C). The depolymerized cellulose was characterized using FTIR, SEM and UV-VIS spectrophotometer. The salt concentration and temperature had substantial influence on the degree of polymerization (DP) of cellulose and glucose concentration. The glucose concentration was determined by using UV-VIS spectrophotometer by the measuring absorbance at 540 nm. The measurement of specific viscosity was carried out to determine the DP of cellulose. The lower the DP of cellulose indicated the more oligomers were obtained.

Key Words: depolymerization, DP, cellulose, oligomers, glucose concentration

ABSTRAK

Penyahpoiimeran daripada selulosa adalah langkah kritikal untuk mogok selulosa ke oligomers dengan kepanjangan rantai yang berbeza. Selulosa depolymerized menggunakan garam bantuan organik asid-pemangkinan telah disifatkan sebagai satu pendekatan yang hijau dan kos efektif. Natrium klorida yang murah (NaCl) dengan asid oksalik telah diperkenalkan sebagai pemangkin ke dalam sistem refluks untuk melakukan penyahpoiimeran asid-catalyzed daripada selulosa di bawah keadaan tindak balas yang sederhana (105-150^{0}C). Selulosa depolymerized dicirikan menggunakan FTIR, SEM dan UV-VIS spektrofotometer. Kepekatan garam dan suhu mempunyai pengaruh yang besar kepada darjah pempolimeran (DP) daripada selulosa dan kepekatan glukosa. Kepekatan glukosa telah ditentukan dengan menggunakan UV-VIS spektrofotometer oleh keserapan mengukur pada 540nm. Pengukuran kelikatan tertentu telah dijalankan untuk menentukan DP daripada selulosa. Semakin rendah DP menunjukkan lebih oligomers diperolehi.

Kata Kunci: penyahpoiimeran, DP, selulosa, oligomer, kepekatan glukosa

1.0 Introduction

Waste paper is increasingly recognized as a major environmental issue. According to Gayathri and Rajeswari (2011), the need for paper is expected to increase to 4 kg per person per year. In order to manufacture one tonne of paper board or every one tonne of mill made paper, about 300 trees are cut, and 2.5 to 3.0 tonnes of dry forest based materials are required (Gayathri and Rajeswari, 2011). Paper is all around us but many people did not notice it. Paper comes from many forms such as paperboard, tissue paper, book, index card, receipt and coffee cup sleeve. With increasing population, the need of paper also increases. It was reported that Municipal Solid waste (MSW) consisted of 40% of paper waste (U.S. Environmental Protection Agency, 2014). Martin (2011) reported that over the past 40 years, the world consumption of paper had grown by 400 percent. Paper industries used almost 4 billion trees or 35 percent of the total trees cut around the world to manufacture paper products (Martin, 2011). Unfortunately, paper everywhere caused a serious problem to environment and environmental pollution.

As Adewole (2009) pointed out that waste must be used as a resource. Recycling of the paper can save the landfill space. According to the report published by the U.S. Environmental Protection Agency (EPA) in 2011, paper waste caused the worst pollution to water, air and land. Paper is a solid waste and most of it will be buried in the landfill because landfill is the simplest, cheapest and cost effective method to dispose the trash. Although paper is biodegradable but when it is disposed in the landfill site, it breaks down and rots away and eventually produces methane which is a very strong greenhouse gas. Besides methane, there are some traces levels of gases like carbon dioxide, hydrogen and nitrogen are being generated during the degradation process (Aljaradin and Persson, 2012). Landfill gas emission had

caused climate change, environment pollution and effect human health. Recycling paper is a better way to save natural resources but not all the paper can be recycled. Moreover, recycled paper products are more expensive than virgin paper because they need a lot of energy resources.

Paper is a renewable resource and cellulose is the major components of paper wastes. Since the raw material for making paper is the cell wall of higher grade plants, the major components of paper are lignin, cellulose and hemicelluloses. Cellulose $(C_6H_{10}O_5)n$ is the natural polymer and biological macromolecules constituting of thousands of glucose units (Wu and Cheng, 2005). Cellulose is currently being used mostly for paper manufacture and bioethanol production but is also being used in the production of artificial fibers (cellulose acetate), plastics (cellulose nitrate), explosives (nitrocellulose), thickeners and gelling agents (cellulose ethers such as carboxymethylcellulose, hydroxyethylcellulose and hydroxypropylmethylcellulose) (Zabaleta, 2012). Thus, the effective utilization of cellulose to produce biofuels has received attention in both academic circles and industry. In this process, an important focus is the depolymerization of cellulose to simple reducing sugars, such as glucose, fructose, xylose, and some partially depolymerized dimers, trimers, and other oligomers (Zhang *et al.*, 2011).

According to Santos *et al.* (2010), sequence of glucose monomers can be found in cellulose. Degree of polymerization (DP) is defined as the number of monomer units in a polymer. The average number of units of glucose in cellulose chain can be determined by the degree of polymerization (Santos *et al.*, 2010). Wang (2000) stated that the average degree of polymerization of cellulose is between the range of 3000 to 15000 depending on the source and is about 10000 in wood. Santa et al. (2010) reported that the purpose of determine the DP

is to evaluate the quality of the paper used. The measurements of specific viscosity were carried out to determine the DP of cellulose (Shlieout *et al.*, 2002). The cellulose has higher DP means it has greater resistance to tensile and other forces (Wang, 2000). Kleinebudde *et al.* (2000) investigated the influence of the DP of cellulose materials during homogenization and spheronization process. They found that higher DP cellulose showed larger particle size after homogenization than the lower DP cellulose. Shlieout *et al.* (2002) stated that greater water adsorption was showed in higher DP cellulose. The main goal of this study is to depolymerize cellulose derived from paper wastes into oligomers of various chain lengths under mild conditions. Such oligomers are potential feedstock for the production of biofuels and functional chemicals.

1.1 Objectives of study

I. To isolate and characterize regenerated cellulose from paper wastes.

II. To depolymerize regenerated cellulose into oligomers.

III. To characterize depolymerized cellulose fragments or oligomers.

2.0 Literature review

2.1 Acid-catalyzed depolymerization of cellulose

The method of acid catalyzed hydrolysis has been used in the 19th century, with commercial applications from the 20th century (Carvalheiro *et al.*, 2008). Schuth *et al.*(2012) reported that cellulose was subjected to a mechanical treatment in the presence of different inorganic acids such as nitric acid, hydrochloric acid and phosphoric acid and/or organic acid, for example, benzenesulfonic acid, nitrobenzenesulfonic acids and oxalic acid. Cellulose was depolymerized into water-soluble products without obtained any by-products. Becker *et al.* (2001) reported successful depolymerization of cellulose ether in the form of an acid slurry. According to Stein *et al.* (2010) dicarboxylic acids such as oxalic acid, are active catalyst for the depolymerization of cellulose at a high temperatures to form oligomers and glucose. Rinaldi *et al.* (2008) reported that cellulose depolymerization was carried out over solid catalysts in the solvent of 1-butyl-3-methylimidazolium chloride ([bmim] Cl). Dutta (2012) reported that a suitable acid-catalyst could improve the selectivity of biomass conversion. Besides, Shimizu and Satsuma (2011) stated that solid-acid catalyst is one of the technologies to establish environmental catalytic processes. Trifluoroacetic acid (TFA) is also used to depolymerize cellulose at 0^0C in not more than 2 hours and the majority of TFA are recycled through vacuum evaporation. A highly amorphous cellulose sample is prepared when the residual of TFA was removed by washing the cellulose with water (Shimizu and Satsuma, 2011). Klemm (1998) stated that, there are three step processes consisting in the acid hydrolysis of a glycoside in an aqueous medium. The fast formation of a corresponding acid by addition of a proton was formed initially and then the formation of pyranosyl cation

followed by the addition and heterolytic cleavage of a water molecule, thus replacing the OR group by a hydroxyl group and replacing H^+ ion.

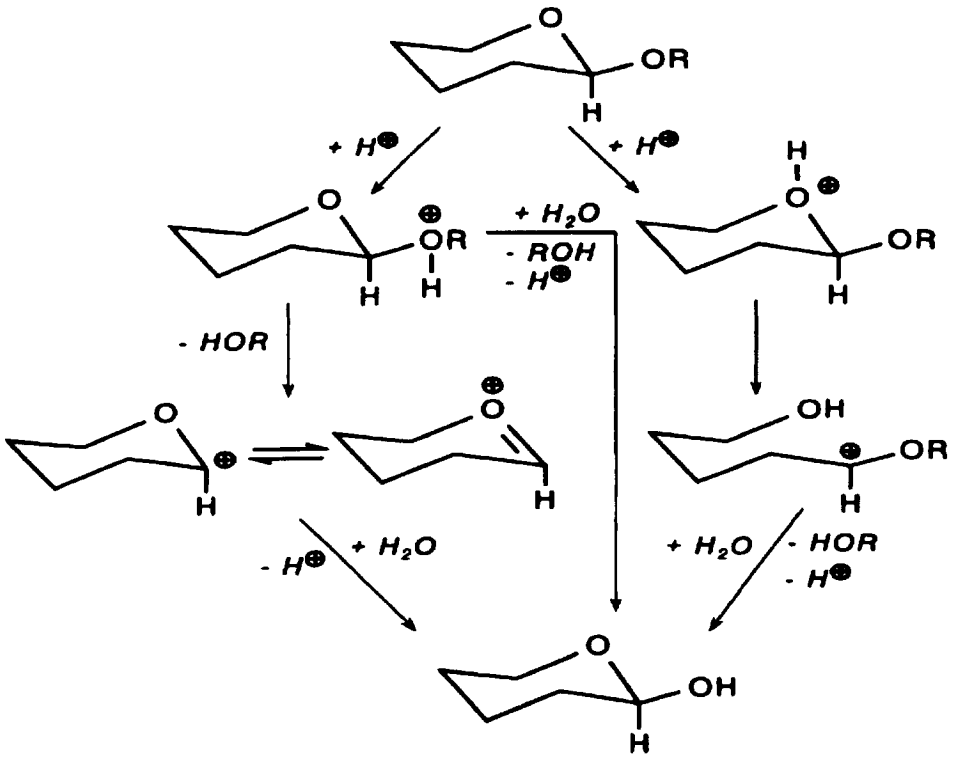

Figure 2.1: Mechanism of acid-catalyzed hydrolysis of a glycosidic linkage pathway through pyranosyl cation (Philipp *et al.*, 1981)

2.2 Dissolution of cellulose in ionic liquids

According to Frone *et al.* (2011), using ionic liquids to depolymerize cellulose are environmentally preferable solvents and bio-renewable feed stocks. Cellulose can be easily depolymerized by using ionic liquid with addition of ethanol, water or acetone (Frone *et al.*, 2011). Sun *et al.* (2012) reported that series of heteropolyacid (HPA) ionic liquids $[C_4H_6N_2\{CH_2\}_3SO_3H]_{3-n}H_nPW_{12}O_{40}]$ to catalyze one-pot depolymerization of cellulose into glucose. The products and catalyst were easily separated, and the catalyst $[MIMPSH]_nH_{3-N}PW]$ could be reuse without effecting the performance (Sun *et al.*, 2012). Liu *et al.* (2013) stated

that acidic ionic liquid functionalized polymer PDVB-SO_3H-[C_3vim]-[SO_3CF_3] produced many nanoporous structures, unique capability and strong acid strength for the crystalline cellulose into sugars in ionic liquid. Past few years, Su *et al.* (2011) reported that a catalytic system involving primary metal chloride, Copper (II) chloride ($CuCl_2$) paired with a second metal chloride, such as Palladium (II) chloride ($PdCl_2$), Chromium (II) chloride ($CrCl_2$) or Chromium (III) chloride ($CrCl_3$) in an ionic liquid solvent, 1-ethyl-3-methylimidazolium chloride [EMM]Cl were accelerate the rate of cellulose depolymerization under suitable condition. Swatloski *et al.* (2002) stated that the solubility of cellulose was decreased and precipitated due to the presence of water in the ionic liquid. Moreover, ionic liquid has been proven to be useful as a non-derivatizing solvent for cellulose. Low vapor pressure, tunable hydrophobic and hydrophilic character and range of viscosity and gas solubility are the properties of the ionic liquid (Zhao *et al.*, 2000). Swatloski *et al.* (2002) stated that ionic liquid contain halide anions and are used as non-derivitizing solvents for cellulose. Besides, they also found that the ability of ionic liquid to dissolve cellulose varies significantly with the size and polarizability of the anion present and also the nature of cation (Swatloski *et al.*, 2002).

2.3 Enzymatic hydrolysis

In the paper industry, the enzymatic hydrolysis of waste paper is desirable from the standpoint of green and clean processing, although the process presents challenges as a slow reaction rate and low process efficiency. This is mainly due to the high crystallinity of cellulose, the present of lignin, low specific area of the material, and the complexity of cellulases as multicomponent enzyme system (Vynios *et al.*, 2009). Kim *et al.* (2007) reported that cellulose can be converted into fermentable sugars by enzymatic hydrolysis. According to

Demers *et al.* (2012), cellulose enzymes were used to break down the cellulose in the wood shavings, apple pomace and swithchgrass feed stocks. The enzymatic hydrolysis reaction is carried out with enzymes which act as catalyst to break down glycosidic bonds of cellulose (Demers *et al.*, 2012). Galbe and Zacchi (2002) reported that the cellulose successfully hydrolyzed with three different types of cellulose enzyme: betaglucosidase, exoglucanase and endogluconase. Wyman *et al.* (2000) stated that glucose is formed through the enzymatic hydrolysis of cellulose. Reese (1976) reported that enzymatic hydrolysis of cellulose to ethanol involved separate operations for pretreatment of biomass and to depolymerize biomass, cellulose by using cellulase. Watson *et al.* (2009) reported that large cellulose enzyme was required to break down the cellulose and decrease the crystallinity of cellulose. Mansfield *et al.* (1997) reported that cellubiose dehydrogenase can reduce the degree of depolymerization of the pulp cellulose. Moreover, they prove that enzyme cellubiose dehydrogenase (CDH) and cellubiose alone can depolymerized cellulose to a greater extent. This is because CDH generated cellobionolactone, which act as an inducer of cellulolytic enzymes while preventing B-glucosidases (Mansfield *et al.*, 1997).

2.4 Thermal degradation

LeVan (1989) reported that, the chemical structure of the wood is changed when exposed to elevate temperatures. The thermal degradation of wood occurred both at high temperatures (>300 °C) and at low temperatures as shown in Figure 2.4.1. Volatile oil, weight loss, reduced strength, and hydroscopic water are some changes of wood chemical structures. Process such as oxidation, dehydration, hydrolysis, decarboxylation and transglycosylation occur via degradation. Cellulose which is the components of wood, shows a decrease in its degree of polymerization when being heat treated at low temperature pathway and water is

also evolved from the oven-dried cellulose. The degree of polymerization of cellulose decrease when the temperature was increased. Then free radicals were also appeared, the rate of thermal degradation increase as heat treatment continues. Glucose is produced when cellulose absorbed enough energy to breakdown of glycosidic linkage (LeVan, 1989).

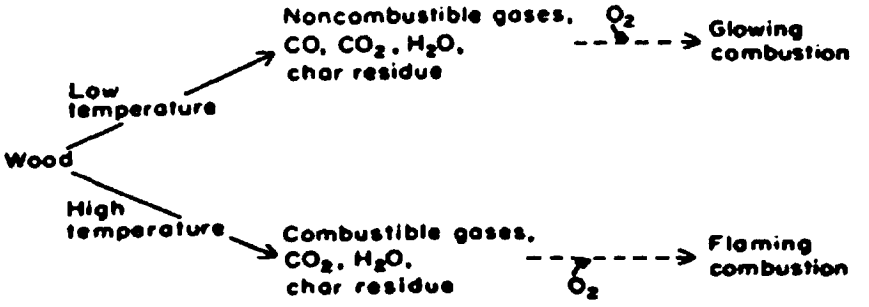

Figure 2.2: Degradation of wood by low-temperature and high-temperature pathways (LeVan, 1989).

Koll *et al.* (1991) reported that depolymerized cellulose by thermal degradation in tetraethyleneglycol dimethylether as a high boiling and inert solvent to give water-soluble oligomers with a terminal anhydrosugar unit. According to Huang (2012), cellulose tri-stearate was synthesized from trifluoroacetic anhydrided, strearic acid and microcrystal cellulose and occurred as weight loss when the degradation of cellulose tri-stearate in argon. Ming *et al.* (2006) stated that there are two types of reactions occurred in thermally decomposed. At lower temperatures, there is gradual degradation which includes depolymerization, oxidation, dehydration, constitutions of carbonyl and carboxyl groups and developed of carbon monoxide and carbon dioxide lastly resulting in a carbonaceous residue forms. At higher temperatures, cellulose is break down into a tarry compound with laevoglucose as the major constituent (Ming *et al.*, 2006).

2.5 Alkali treatment

According to Carvalheiro *et al.* (2008), alkali pretreatment increase cellulose digestibility. Wang *et al.* (2008) and Fengel *et al.* (1995) reported that 8 percent to 26 percent of aqueous sodium hydroxide (NaOH) solution caused the structural changes of the molecular and supramolecular cellulose. Mittal *et al.* (2011) reported that the aqueous NaOH and anhydrous liquid ammonia treatments changed the crystalline configuration of cellulose. The function of ammonia is to swell cellulose and alter its crystal lattice and react with hydroxyl groups after breaking the hydrogen bonds (Mittal *et al.*, 2011). Ozturk *et al.* (2009) also reported that, the interaction between the cellulose and alkali metal hydroxides, for example, sodium hydroxide (NaOH), lithium hydroxide (LiOH) and potassium hydroxide (KOH) can caused the splitting of lyocell into different numbers of macrofibrils. Mittal *et al.* (2011) stated that different cellulose samples were treated with aqueous NaOH to investigate the changes in cellulose crystal structure. Carvalheiro *et al.* (2008) stated that the process of alkali hydrolysis induced swelling leading to increase in internal surface area. Furthermore, alkali caused the degree of polymerization of cellulose to decrease and crystallinity occurs with a consequent separation of structural linkages between lignin and carbohydrates (Carvalheiro *et al.*, 2008).

2.6 Potential application of cellulose depolymerized products

Zhu *et al.* (2006) stated that cellulose derivatives and cellulose composites have great potential in industrial applications such as wool keratin or cellulose composite can be used in the textile industry to produce fibers. The Institute of Process Engineering, Chinese Academy of Sciences and Wuliangyi Corporation in China had participated in a program of manufacture an anti-bacterial fiber by using the cellulose composite technology. Anaerobic degradation of

cellulose by using syntrophic bacteria would be dissimilated cellulose to carbon dioxide (CO_2) and methane (CH_4) (Zhu *et al.*, 2006). Thus it plays an important role in carbon cycling on the planet (Leschine, 1995). Kim *et al.* (2007) stated that enzymatic hydrolysis of cellulose can be converted to fermentable sugars like glucose. Cellulosic biomass has a high potential for biofuel production due to its high sugar content (Tsai *et al.*, 2010). Production of ethanol from cellulosic biomass is very useful as an alternative transportation fuel. Peng *et al.* (2011) stated that nanocrystalline cellulose obtained from acid hydrolysis of cellulose fibers had wide application prospects due to its great physiochemical properties such as high specific strength, high surface area and unique optical properties. Some potential applications of nanocrystalline cellulose are protein immobilisation, nanocomposite films, drug delivery and metallic reaction template (Peng *et al.*, 2011). Frone *et al.* (2011) stated that cellulose nano-fibers have many potential applications in important fields like electronic and electrical industry, packaging, paper industry and textile industry. The polypyrrole-Cladophora cellulose composite can be used as an electrode material in electrochemical industry (Razaq, 2011). He also stated that cellulose like Cladophora cellulose can be used as a tabletting aid for drug delivery, as reinforcement in construction materials and as a thickener to improve the stability and texture of other dispersive system. The main uses of nanocomposites cellulose are coatings and templates, nucleating agent, responsive material and reinforcements (Salajkova, 2012). Besides, Janardhnan and Sain (2011) reported that cellulose microfibrils are used to make ultralight composite materials. Microfibrils also can be applied in packaging materials and in traditional paper products (Janardhnan and Sain, 2011).

2.7 Pretreatment of paper waste

2.7.1 Deinking of paper waste

Kemppainen *et al.* (2010) stated that, pulping operations water and deinking chemicals are added to recycled paper to loosen fiber-fiber and ink fiber bonds to ease the process of ink detachment by mechanical action. According to Venditti (2004), paper recycling process by using the flotation deinking method in order to remove the hydrophobic contaminants like ink and toners from the fibers in an aqueous phase. Waste paper is blended in a blender and then waste paper is bleached by pumping air bubbles through the suspension using an aquarium pump (Venditti, 2004). According to El-Shall *et al.* (2005), reagent such as ammonium hydroxide or sodium bicarbonate can be used at room temperature to produce fine bubbles at the ink, fiber and water interface to help in the ink detachment. Conventional deinking by converting waste paper to pulp and contacting the pulp with an alkaline aqueous deinking medium, and chemicals that plays an important role in the ink separations and removal process. Alkali silicate acted as oxidizing bleaching agent was used in the process of wastepaper pretreatment (El-Shall *et al.,* 2005). Yun and He (2013) stated that sodium hydroxide was used as an alkali source in hydrogen peroxide bleaching. Hydrogen peroxide is used to improve the brightness of deinked fibers by reacting with different color carbonyl-containing structures in lignin. Hydrogen peroxide is cheap and effective in alkali aqueous solution (Yun and He, 2013). Hwang *et al.* (1994) stated that method of wastepaper deinking is dependent on the size of ink particles. For small ink particles, wash deinking was used, whereas for big ink particles floatation deinking methods was used. Hwang *et al.* (1994) suggested that deinking solvents such as water-soluble alcohols, esters, aldehydes, organic acids are preferred. Wash deinking method can caused the paper yellowing due to the presence of the residual alkali, presence of both ink and chemicals in the effluent, large consumption of water, low quality of